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(71) Applicant:
Chemische Werke Zell-Wildshausen
GMBH, D-40549 Düsseldorf (DE)

(72) Inventors:
- Born, Gerhard
  47800 Krefeld (DE)
- Brandt, Burkhardt
  33106 Paderborn (DE)
- Krumbiegel, Andreas, Dr. rer. nat.
  68169 Mannheim (DE)

(74) Representative:
Meyer-Roedern, Giso, Dr.
Berheimer Strasse 10-12
69115 Heidelberg (DE)

(54) Agent for reducing chromium (VI) ions in a hydraulic setting compound

(57) An agent for reducing chromium (VI) ions in a hydraulic setting compound, comprising at least 0.02% Sn (II) ions and at most 98.8% lignin sulfonic acid produced according to an electrochemical process.

Description

[0001] The 6-valent chromium compounds, e.g. chromium (VI) oxide, are toxic and act as strong oxidation agents which are caustic to skin and mucous membranes. Chromate allergies occur, e.g., the well-known bricklayer's eczema.

[0002] According to the prior art, systems already exist, which will reduce water-soluble compounds of chromium (VI), e.g., in the cement matrix. They are essentially based on the reducing properties of a cation from subgroup elements. The reducing effect of iron (II) ions has been particularly emphasized.

[0003] Of course, it can be observed that chromium (VI) can only be reduced with great difficulty in a strongly alkaline solution. Thus, after a longer residence time, the concentration of the chromium (VI) ions increases again. Similar effects are also observed for other systems. The difficulties intrinsic to the reduction of Cr (VI) ions are the following.

[0004] The redox behavior of chromates:

[0005] The characteristic property of chromates is their strong oxidizing effect, since upon addition of oxidizable substances they have a great tendency to proceed further to the stage of three-valent chromium:

$$CrO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Cr^{3+} + 4\,H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6\,e^- \Leftrightarrow 2Cr^{3+} + 7H_2O$$

[0006] The oxidation effect is particularly high in acid solution and greatly decreases with increasing basicity. From this results the problem of the effectiveness of agents which can be utilized for chromium (VI) reduction, e.g., in the cement matrix (pH approx. 14).

[0007] It will be shown on an example why no permanent and sufficient chromate reduction can be provided with iron (II) ions:

1.) Equilibrium reaction:

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$$

The described equilibrium provides an electron, which is utilized for the reduction of chromium (VI) to chromium (III).

2.) On the other hand, the following equilibrium exists between chromium (III) and chromium (VI):

$$2Cr^{3+} + 7H_2O \Leftrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$$

Chromium (III) ions are very stable against oxidation and reduction in acid solution, but with increasing basicity, this stability decreases. This applies particularly to the cement matrix. This means that a slow oxidation of chromium (III) to chromium (VI) occurs based on the equilibrium. This back-reaction can no longer be influenced by the iron ions, since these have already been eliminated by the application of $Fe(OH)_3$. Therefore, the reducer with iron (II) ions absolutely does not fulfill the stated objective of chromate reduction.

[0008] Additional disadvantages of the iron (II) reducer result in the application. In practice, iron (II) is utilized in the form of a sulfate for the reduction of the chromate in cement. Since such a solution would be subject to acid hydrolysis, it is utilized as a powder. In this way, the iron (II) is converted to iron (III) via the oxygen in air. Thus, the [use of] iron (II) sulfate requires a particular attentiveness and special conditions for its application. In practice, this chemical is packed in bags that dissolve in water and is mixed into the cement system by addition. In this way, two disadvantages arise, which stand in the way of the objective of unequivocal chromate reduction:

--In this treatment, a large amount of Fe (II) is converted to Fe (III).
--The Fe (II) is mixed in. Because of this, there is no statistically equal distribution over the entire system, i.e. an exact metering is not possible. Another contamination with Cr (VI) ions of those persons who work with this cement, which has been treated in this way, cannot be excluded.

[0009] Since a significant increase of oxidative modifications of the bases will be observed in DNA upon administration of Fe (III), the latter has been described as a tumor inducer (Dekant, Vamvakar: Toxikologie für Chemiker und Biologen [Toxicology for Chemists and Biologists], 1994, Spektrum, pp. 282, 283).

[0010] Another possibility for chromate reduction is organic systems, such as, e.g., aldehydes, and specific heterocyclic compounds. For example, chromium (VI) is reduced to chromium (III) by menthanol. Pyridine is more effective. These substances cannot be utilized, however, for many reasons. The reasons include the quantity used, their low stability in the cement matrix as well as toxicological and economic considerations.

[0011] There have been considerations of utilizing lignin sulfonates from the pulping process as chromate reducers, which serve, on the one hand, as complexers of cations, e.g., Fe^{2+}, and, on the other hand, contain aldehyde groups of the most varied origin as well as heterocycles.

[0012] Unfortunately, it was established that lignin sulfonates from the pulping process cannot sufficiently fulfill this requirement, i.e., that they are not effective enough to achieve the required value of 2 ppm of chromium (VI). The reason for this lies in the structure of the indicated lignin sulfonates. After the pulping process, lignin sulfonates represent an irregular, random, three-dimensional network. It results from this that sometimes more active groups and sometimes less active groups are present purely randomly on the surface of the lignin system. Thus, the factor by which means the chromate ions will be reduced is never constant and also is insufficient in overall total sum.

[0013] However, if lignin sulfonates from the pulping process are treated by an electrochemical method, as is known from the German Patent P 43 06 260.1-09 and the European Patent No. 0 687,247 (Application Number 94 90 82 58.0-2104), then one obtains reproducible lignin sulfonic acids (LSA) adapted to this application. For chromate reduction, lignin sulfonic acids with an average molecular mass distribution of 1,000 to 25,000 are produced. The lignin sulfonic acid is made up in such a way that, for the most part, different aldehyde groups (of non-aromatic and aromatic character) as well as heterocyclic and other carbonyl groups are found on the surface of the macromolecule. These groups reduce reduce the fraction of chromium (VI). In the case of the lignin sulfonic acids produced according to the indicated patents, the designated groups are arranged on the surface of the molecule and thus are effective for chromate reduction.

[0014] The lignin sulfonic acid (LSA) system is an excellent dispersion agent and is distributed particularly well, e.g., in the cement matrix. Therefore, all of the chromate ions are reached and the chromium (VI) ions are reduced almost completely due to the molecular mass distribution and the high number of reducing groups in one macromolecule. As is known from the named patents, the LSA products are reproducible.

[0015] Nevertheless, it has been established by investigations that neither iron (II) compounds, nor products based on lignin sulfonate nor other known compounds can reduce the water-soluble content of Cr (VI) ions in the cement matrix, permanently and economically, to a required value of less than 2 ppm.

[0016] It is possible, however, to reduce the content of water-soluble chromate by Sn (II) ions in a long-lasting manner, e.g. in the cement matrix, and therefore to clearly reduce the chromate values to below the 2 ppm limit.

[0017] Tin II represents a strong reducing agent, since it has the tendency to be converted to its four-valent stage:

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

[0018] In addition, in strongly basic solution, tin II forms an amphoteric tin II hydroxide, which does not lose its mobility even in the case of very high pH values. Thus, the chromium VI is completely reduced to chromium III:

$$2Cr^{6+} + 3Sn^{2+} \rightarrow 2Cr^{3+} + 3Sn^{4+}$$

Table

Test cement containing 22 ppm of water-soluble chromate (Cr VI)

0.04% Fe (II) reduces the chromate content to 15 ppm = Reduction effect: 32%

0.04% Sn (II) reduces the chromate content to 1.7 ppm = Reduction effect: 92.3%

[0019] Additional synergistic effects can be achieved for the chromate reduction by the use of lignin sulfonic acid (LSA) in conjunction with Sn (II) ions in the cement matrix. In this way, the reducing properties of Sn (II) are substantially improved. The compound tin/lignin sulfonic acid reduces the water-soluble Cr (VI) content in the cement matrix to 0 ppm. In addition, in contrast to Fe (II) and its compounds, the Cr (III) content generated by the chromate reduction is stably maintained over a long period of time.

Standard formulation:

[0020]

1.6%	Sn II ions
98.4%	Lignin sulfonic acid (LSA)

[0021] The metering of the standard formulation for reducing the chromium (VI) content to below 2 ppm can be derived from the following table. The chromium content of the cement and the quantity of standard formulation referred to the cement fraction are indicated.

Table

Chromate content in the cement	Quantity of reducer
22 ppm	0.45%
18 ppm	0.38%
10 ppm	0.2%
5 ppm	0.1%

[0022] Advantages of the Sn (II) chromate reducer system:

--Sn (II) is toxicologically completely unobjectionable.

--Application as a liquid permits a precise metering, which is fine-tuned to the respective chromate content in the individual case.

--Lasting reduction of the Cr (VI) content to a value of < 2 ppm, which is stable over the entire matrix.

--The consequence is that persons will no longer be contaminated with Cr (VI) when working with substances treated with Sn (II) reducer and thus will no longer become ill with chromatosis.

--The Sn (II) reducer can also be utilized as a powder if necessary.

Application of the Sn (II) reducer:

[0023] The aim of the construction industry is to produce hydraulic or latent hydraulic setting compounds. These compounds may be contaminated with Cr (VI) ions from the most varied sources. Such compounds are essentially comprised of binders, aggregates, additives and water. The sources of contamination are to be found primarily in sand from the metallurgical industry and in fly-ash.

[0024] The application of the described chromate reducer can be produced in the most varied manner. It is therefore conceivable that aerosols of the Sn (II) reducer can be used in order to reduce the Cr (VI) content in fly-ash, or it can be used in the form of a liquid or a powder in grinding processes. In addition, the Sn (II) reducer can be utilized on site, i.e., directly in the preparation of the hydraulic setting compounds (wet or dry). The Sn (II) reducer can be incorporated in any additive in order to produce a synergistic effect with the additive, namely to reduce the Cr (VI) content as described.

[0025] Whatever the manner by which the Sn (II) reducer is applied, it reacts with water-soluble Cr (VI) ions according to the manner described and thus permanently and clearly reduces the Cr (VI) content to below the prescribed value of 2 ppm. Basically, the Sn (II) reducer can be applied wherever Cr (VI) is present in water-soluble form.

[0026] The application can be employed in fly-ash, sand from the metallurgical industry, aggregates, grinding adjuvants, binders, additives, or directly in production, e.g., in ready-mixed concrete or assembly of finished units. Basically, the described chromate reducer can be used wherever water-soluble Cr (VI) ions are present in a system, which leads to a hydraulic setting or latent hydraulic setting compound. The chromate reducer can be precisely metered.

Patent claims

1. An agent for reducing chromium (VI) ions in a hydraulic setting compound is hereby characterized in that it contains at least 0.02% Sn (II) ions.

2. The agent according to patent claim 1, further characterized in that it is comprised of at least 0.02% Sn (II) ions and at most 99.98% lignin sulfonic acid (LSA), which is produced according to the electrochemical method of the German Patent P 43 06 260.1-09 or of the European Patent No. 0 687,247 (Application Number 94 90 82 58.0-2104).

3. The agent according to patent claim 2, further characterized in that it is comprised of 1 to 60% Sn (II) ions and the remainder up to 100% of lignin sulfonic acid (LSA).

4. The agent according to patent claim 2, further characterized in that it is comprised of 1.6% Sn (II) ions and of 98.4% lignin sulfonic acid (LSA).

5. The agent according to one of claims 1 to 4, further characterized in that it is of powder form.

6. The agent according to one of claims 1 to 4, further characterized in that it is a liquid.

7. Use of an agent according to one of patent claims 1 to 6 in the production of the binding agent of a hydraulic setting compound, hereby characterized in that the agent is added to an initial substance or a substance to be ground or additive or grinding adjuvant of the binding agent, particularly sand from the metallurgical industry or fly-ash.

8. Use of an agent according to one of patent claims 1 to 6 in the production of a dry hydraulic setting compound, hereby characterized in that the agent is added to a binding agent or to an aggregate or to an adjuvant (additive).

9. Use of an agent according to one of patent claims 1 to 6 in the mixing of a hydraulic setting compound, hereby characterized in that the agent is added to a binding agent or to an aggregate or to an adjuvant (additive) or to the mixing water.